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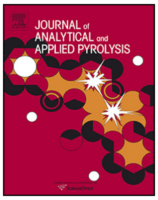

Evaluation of the thermal and environmental stability of switchgrass biochars by Py–GC–MS

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ABSTRACT

Flash pyrolysis GC–MS (Py–GC–MS) was applied to the characterisation of 35 biochars synthesised from switchgrass with a bench scale reactor at different temperatures (400–700 °C) and residence times (1–20 min). Py–GC–MS data were compared with the molar hydrogen to carbon ratios (H/C) taken as an index of the charring intensity along with other parameters. O/C ratios and biochar yields were directly correlated with H/C ratios, while ash, total carbon and pH were inversely correlated. A weak inverse correlation was found between polycyclic aromatic hydrocarbon (PAH) concentrations and H/C. The intensity and variety of pyrolysis products in the pyrograms decreased with decreasing H/C ratios, so that pyrograms of highly carbonised biochars (H/C < 0.4) were principally characterised by benzene, pyrrole, toluene, C_2–benzenes, benzonitrile, benzofuran, naphthalene, diphenyl, phenanthrene. These compounds were taken as representative of a highly carbonised, but thermally labile portion of biochar. Their relative abundance (% charred) with respect to pyrolysis products representative of weakly charred lignocelluloses was linearly correlated with H/C ($R = -0.93$). Good correlations were found between specific pyrolysis product ratios and H/C ratios. Four selected biochars were mixed with soil and subjected to short respiration rate experiments (220 days). Biochars with a moderate (H/C ~ 0.6) and high (H/C ~ 0.4) degree of carbonisation produced different pyrograms, but exhibited the same degradation rates, with a much lower conversion into CO_2 than the weakly carbonised sample (H/C ~ 1.5) characterised by a high proportion of hemicellulose/cellulose markers in the pyrolysate.

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1. Introduction

Biochar is a carbonaceous solid material artificially synthesised from biomass with the purpose to enhance soil properties and carbon sequestration. Explorative studies highlighted a series of advantages in the use of biochar as soil amendment that included increased soil fertilisation, valorisation of agrochemical byproducts, storage of carbon, reduced greenhouse gas emissions along with possible limitations and drawbacks [1–6]. Because of the growing interest captured by this material, a plethora of analytical techniques have been applied to investigate its chemical structure and undoubtedly GC–MS is the master technique for the determination of individual organic compounds formed during charring and sorbed onto the carbonaceous matrix. GC–MS was applied to the analysis of polycyclic aromatic hydrocarbons (PAHs) [7–10], polychlorinated organic compounds [7], and volatile organic compounds [11,12] in chars obtained from different sources.

The chemical information affordable by GC–MS was extended to non-volatile components susceptible to be thermally fragmented into volatile compounds by means of flash pyrolysis (Py) [13–17]. When charcoals were subjected to Py–GC–MS the resulting GC–MS traces (pyrograms) were featured by peaks associated with benzene, toluene, naphthalene, biphenyl, dibenzofuran and benzonitrile [13]. These pyrolysis products were assumed to represent the charred fraction rich of aromatic structures that occurs in a thermally labile form in the carbonaceous matrix. In addition, pyrolysis product ratios representing the relative abundance of alkylated and parent compounds (e.g., benzene/toluene peak area ratio) were proposed as indicators for the presence of saturated alkyl bridges between polyaromatic structures and hence a measure of the charring intensity [14]. On a quantitative basis, Py–GC–MS applied to a set of biochar samples produced from

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the same feedstock at increasing temperatures (thermosequence) showed that the total GC peak areas of the evolved pyrolysis products decreased with increasing charring intensity, whilst the relative peak area (% charred) of products associated with charring (aromatic hydrocarbons, benzofurans, and benzonitriles) increased [15]. Highly polycondensed aromatic moieties cannot be cracked into volatile compounds and pyrolysates of extremely carbonised biochars were barely detectable by GC–MS. In contrast, intense pyrograms featured by pyrolysis products preserving the chemical functionality of hemicellulose, cellulose and lignin (e.g. pyranones, furaldehydes, methoxyphenols) were revealed in the pyrograms of chars obtained at low temperatures [15].

Therefore, total peak areas and % charred were proposed as indices of the charring intensity in accordance to the results obtained with other analytical techniques applied to the same samples, such as hydrogen pyrolysis (HyPy) with carbon isotope ratio [18], and Fourier transform infrared spectroscopy (FTIR) [16].

The widespread validity of these Py–GC–MS indices (total peak area or pyrolysis product yield, % charred, pyrolysis product ratios) was tested through the analyses of biochars from different feedstock and process conditions [17]. The estimated yield of pyrolysis products was correlated with volatile matter, a parameter proposed for the labile charred fraction [19], while the % charred was inversely correlated with the elemental O/C ratio, a measure of charring and environmental persistence [20]. However, correlations between Py–GC–MS data and the various biochar parameters were not very strong, probably because of the great variability in the biochar sources.

Nevertheless, the knowledge of the thermal behaviour of biochar is of great interest because it may help in predicting the environmental stability of biochar and its ability to store carbon more efficiently than fresh biomass. To this purpose, indices have been proposed based on elemental [20] and thermal analysis [19,21]. As above illustrated, Py–GC–MS is able to provide molecular indices of the thermal stability, however, a few studies have been published aimed at comparing these indices to those arising from aerobic degradation [17,22]. The CO_2 production from incubation experiments was found to be high for biochars producing pyrograms characterised by the presence of lignocelluloses markers [17]. However, even highly carbonised biochar producing a Py–GC–MS trace characterised by the presence of aromatic hydrocarbons and the lack of lignin/carbohydrate markers can induce respiration when applied to soil [23].

In general, more data are necessary to evaluate the potential and consistency of Py–GC–MS for the characterisation of the thermal and environmental stability of biochar using molecular markers. The goal of this study was to provide a comprehensive comparison between molecular analysis by Py–GC–MS and bulk analysis on a large set of biochar samples produced from the same feedstock and the same pyrolysis unit. Different process conditions, charring temperature and residence time, were utilised to obtained biochars with different degrees of charring. Then, a sub-set of samples characterised by different Py–GC–MS traces were subjected to CO_2 respiration tests. Switchgrass (*Panicum virgatum*) was selected as biomass because of its importance in energy crops where pyrolysis to produce bioenergy is coupled with carbon sequestration [24–26].

2. Experimental

2.1. Biochar production

Biochar samples were synthesised by pyrolysis of switchgrass (*P. virgatum*, air dried at 60 °C, milled and sieved at 2 mm) using a fixed bed tubular quartz reactor (length: 650 mm, internal diameter 37 mm) placed into a refractory furnace. Switchgrass samples (about 3 g of biomass) were uniformly placed onto a sliding quartz boat, under a nitrogen flow of 1500 $cm^3 min^{-1}$. When the temperature inside the reactor, measured with a thermocouple, reached the selected value, the boat was pushed into the oven. Pyrolyses were performed at different temperatures, in the 400–700 °C range, with increments of 50 °C. After a given residence time (1, 2, 5, 10 or 20 min), the quartz boat was withdrawn from the heated zone and cooled at ambient temperature under nitrogen in order to avoid possible char oxidation. Then, biochar was weighed and kept in closed vials before analysis. Overall 35 biochar samples were obtained and named according the synthesis conditions. As an example, biochar 500/10, is the biochar synthesised at 500 °C for 10 min.

2.2. Chemical analysis

Elemental composition (HCNS) was determined by combustion using a Thermo Scientific Flash 2000 series analyser. Ash was determined as the residual mass left after exposure at 600 °C for 5 h. The oxygen content was calculated from the mass balance: $\%O = 100 - \%(C + H + N + ash)\%$. A mixture of biochar with deionised water at 1:10 wt/wt ratio was prepared, thoroughly mixed and pH measured at room temperature with a digital pH meter (HI 98103, Checker®, Hanna Instruments).

Analyses of PAHs were conducted as described in [10] on about 0.5 g of biochar spiked with 0.1 mL of surrogate PAH mix (Supelco for EPA 525 containing acenaphthene-d_{10}, phenanthrene-d_{10} and chrysene-d_{12} 5 $\mu g\, mL^{-1}$ each in acetonitrile) and soxhlet extracted with acetone/cyclohexane (1:1, v/v) for 36 h. The solution was filtered, added with 1 mL of *n*-nonane (keeper), carefully evaporated by rotatory vacuum evaporation at 40 °C and cleaned up by solid phase extraction onto a silica gel cartridge before analysis with a Agilent HP 6850 GC coupled to a Agilent HP 5975 quadrupole mass spectrometer; GC–MS conditions were those detailed in [10]. Recovery of surrogated PAHs was determined with respect to the internal standard tri-*tert*-butylbenzene.

2.3. Py–GC–MS

Py–GC–MS analyses were performed using an electrically heated platinum filament CDS 1000 pyroprobe valved interfaced to a Varian 3400 GC equipped with a GC column (HP-5-MS; Agilent Technologies 30 m × 0.25 mm, 0.25 μm) and a mass spectrometer (Saturn 2000 ion trap, Varian Instruments). GC thermal program: 35 °C to 310 °C at 5 °C min^{-1}; MS conditions: electron ionisation at 70 eV, full scan acquisition in the 10–450 *m/z* interval. A quartz sample tube containing a weighed amount of sample in the interval of 5 mg (biochars produced at residence times of 5–20 min) to 0.5 mg (biochars produced at residence times of 1–2 min) was inserted into the Py–GC interface (300 °C) and then pyrolysed at 900 °C (set temperature) for 100 s with helium as carrier gas (100 $mL\, min^{-1}$). The internal standard addition used in [17] failed to provide reliable results, probably because of the different interface used in this study. Single point external calibration (1 μL of 1000 $mg\, L^{-1}$ ethyl benzoate solution in acetonitrile) was performed to estimate the detector response factor. The yield ($\mu g\, mg^{-1}$) was expresed as the quantity of each pyrolysis product evolved from a weighed amount of analysed biochar and was calculated from the GC peak area in the mass chromatogram at the *m/z* of the characteristic ion in the mass spectrum [17] and the response factor relative to ethyl benzoate. A unitary relative response factor was assumed for all the quantified compounds on the basis that our objective was to determine relative quantities, not the absolute yields of the various pyrolysis products similarly to other studies [14–17].

A set of 34 pyrolysis products were quantified as markers of polysaccharides (holocellulose) (hydroxyacetone,2,5-dimethylfuran, furaldehyde, furfuryl alcohol, 2-cyclopentanedione, 2-hydroxymethylenetetrahydrofuran-3-one, 3-hydroxy-2-methylcyclopentenone, 5-hydroxymethyl-2-furaldehyde);lignin (phenol, 4-methylphenol, guaiacol, 4-ethylphenol, cathecol, 4-vinlylphenol, 4-methylguaiacol, 4-vinylguaiacol, syringol, 4-methylsyringol, *trans*-isoeugenol, 4-vinylsyringol, 4-propenylsyringol); charred biomass (benzene, pyrrole, toluene, ethylbenzene, *m*/*p*-xylene, styrene, *o*-xylene, benzonitrile, benzofuran, methylbenzofurans (three isomers), naphthalene, phenanthrene [15,17].

2.4. Biodegradation in soil

Aerobic degradation tests were performed with the method described in [27] based on ASTM [28] on four biochar samples (500/1, 400/20, 700/1, 600/5) mixed with a temperate sandy-loamy soil collected in the coastal area called *Piallassa Baiona*, nearby Ravenna, Italy (A horizon, 34.9% sand, 52.4% silt, 12.7% clay; moisture holding capacity 29.5%, pH 8.2). In each test, 300 g of soil (atomic C/N ratio brought to 15/1 with ammonium phosphate solution, sieved to 2 mm particle size) were mixed with 5.00 g of biochar and introduced in a 2 L vessel, containing a beacker with 20 mL 0.4 M KOH solution. The moisture holding capacity of soil was brought to 90% with deionised water before adding biochar and a beaker containing 20 mL deionised water was introduced into each vessel to maintain constant humidity conditions. The vessels were sealed air-tight, and kept in darkness at 20 ± 3 °C for 115 days.The amount of evolved CO_2 was determined by titrating the KOH solutions with 0.25 M HCl. The frequency of titrations ranged from daily to weekly depending on the degradation rate, so that the O_2 content of the vessel (about 19 mmol) never fell by more than 10% in the interval between subsequent titrations. Blank experiments were carried out at the same conditions, using soil without any additional carbon source. Possible variations due to initial wetting conditions [29] were assumed to be compensated by blank correction. Each test (and blank) was run in triplicate. The net cumulative CO_2 loss of biochar was calculated by difference from the treated and untreated soils.

2.5. Statistical analysis

Reproducibility was determined by triplicate runs of each parameter in different days and assumed to be representative to all the data set. Percent relative standard deviations (% RSD) were the followings: biochar synthesis yields (400/20) ± 5.8%; Py–GC–MS (biochar 500/20): yields ± 26%, % charred ± 3.2%, compound ratios: benzene/toluene ± 12%, toluene/naphthalene ± 7.1%, *m*/*p*-xylenes/naphthalene ± 23%, benzofuran/naphthalene ± 8.4%. Recovery of surrogate PAHs was (mean ± %RSD for all the data set): 75% ± 13%, 78% ± 11%, 88% ± 12% for perdeuterated acenaphthene, phenanthrene and chrysene, respectively. PAH analysis was run in duplicates for eight biochar samples, the mean %RSD for total PAHs was 9.8% and 24% for each individual PAH. In the case of respiration experiments, the CO_2 production activities were arithmetic means of triplicate soil samples. Two parameters were said to be correlated when the absolute value of the linear (Pearson) correlation coefficient R was larger than 0.45 (the critical value at the level of significance $p = 0.01$ for two tailed test with 30 degrees of freedom) [17].

Multivariate statistical analysis (Principal Component Analysis, PCA) was performed by Matlab software 2010 (Mathworks, Natick, MA).

3. Results and discussion

3.1. Chemical characteristics

In this study, several charring temperatures and residence times were selected in order to obtain chars with a range of chemical characteristics (Table 1). The degree of carbonisation of chars is generally expressed by molar H/C [22,30] or O/C ratios [20,31]. The H/C ratios here investigated chars ranged from 1.54 (400/1) to 0.25 (700/20) and were strongly correlated with molar O/C ratios ($R = +0.97$, Table 2) in accordance to the loss of oxygenated functionalities with increasing carbonisation [32]. Because of this strong correlation, the degree of thermal alteration could be expressed by both H/C or O/C ratios. The use of O/C ratios was utilised to differentiate environmental carbonaceous materials, moreover its determination by dispersive X-ray spectrometry coupled with scanning electron microscopy (SEM/EDX) can provide further information on the spatial distribution in particles and a better evaluation of oxygen associated with organic matter through the analysis of metals [31]. In the specific case of biochar, H/C ratio (or H/organic C) was proposed as one of the criteria to assess the basic utility of this material [33,34]. Based on this criterion and the fact that the oxygen content was calculated by difference from other parameters, we adopted the H/C ratio as an index of thermal alteration for the purpose of data comparison.

Table 2 shows that H/C ratios were inversely correlated with ash ($R = -0.96$) and concomitantly with pH ($R = -0.93$). These trends are in line with literature data for similar biomass [30]. The concentrations of PAHs ranged between 0.23 (450/1) and 2.1 $\mu g\, g^{-1}$ (700/10), thus always below the levels recommended by IBI [33] or EBC (4–12 $\mu g\, g^{-1}$) [34]. PAH levels tended to increase with decreasing H/C ratios, however, the correlation was not very strong ($R = -0.77$), indicating that a multitude of factors could influence the occurrence of PAHs in biochar [35]. In fact, different trends were reported in the literature [7,9,35], such as decreasing or increasing PAH concentrations with increasing pyrolysis time/temperature for slow and fast pyrolysis, respectively [7], or PAH concentrations peaking at 500 °C in grass biochars produced in the 100–700 °C pyrolysis interval [9]. In the case of biochar obtained from slow pyrolysis (8 h) of switchgrass, PAH concentrations were reported to decrease from 350 to 800/900 °C [7].

The synthesis yields ranged from 16 to 92% (Table 1). The highest yields were obtained with low temperatures (<600 °C) and low residence times (1–2 min), and were nearly constant with residence times equal or larger that 5 min. An average yields of 21 ± 4% in the whole temperature interval of 400–700 °C was calculated. These data compare reasonably with the results from thermogravimetric analyses of switchgrass reporting that mass loss was complete at 550 °C with a residue of 20% [36].

3.2. Py–GC–MS

Some typical pyrograms resulting from Py–GC–MS of biochar samples are depicted in Fig. 1. Samples with high H/C values produced complex pyrolysates with intense peaks assignable to the pyrolysis products of hemicelluose, cellulose or lignin, on the contrary samples with low H/C ratios produced simple pyrograms with weak peaks of aromatic hydrocarbons.

Pyrolysis products selected for quantitation were grouped into three thermolabile class fractions: highly carbonised (charred), weakly carbonised hemi/cellulose and weakly carbonised lignin (see experimental part). The grouping of pyrolysis products into the fraction was specified in Section 2.3.

Switchgrass hemicellulose is mainly composed of arabinoxylans [37], but anhydropentofuranoses (characteristic ions at m/z 57, 73, 86) which are specific pyrolysis products of

Table 1
Chemical characterisation and Py–GC–MS data (last four columns) of biochars. Values of the original switchgrass are reported in “biomass” row.

Sample (°C min^{-1})	H/C (molar)	O/C (molar)	C (wt%)	N (wt%)	Yield (wt%)	Ash (%)	PAH (μg g^{-1})	pH	Py yield (μg mg^{-1})	Holocellulose (%)	Lignin (%)	Charred (%)
Biomass	1.60	0.78	42.5	0.66	n.a.	6.9	n.d.	7.1	15,400	33	58	9.1
400/1	1.54	0.80	44.5	0.35	92.0	1.9	0.34	5.7	7000	39	49	12
450/1	1.52	0.71	46.8	0.34	91.0	2.8	0.23	5.6	6200	33	60	7
500/1	1.49	0.73	46.3	0.31	89.1	2.7	0.31	5.6	6500	39	50	11
400/2	1.45	0.72	47.2	0.35	86.0	1.4	0.66	6	5900	36	49	16
550/1	1.33	0.67	48.4	0.32	68.0	2.8	0.37	6.1	4600	35	53	12
450/2	1.26	0.62	50.2	0.32	60.8	2.9	0.58	6.4	5700	33	54	13
600/1	1.22	0.56	52.1	0.36	53.4	3.3	1.8	6.8	3900	36	45	19
500/2	0.96	0.37	60.1	0.40	37.5	5.4	0.82	7	4100	11	60	30
400/5	0.80	0.28	65.5	0.45	31.4	5.5	1.0	7	1300	4.4	74	21
650/1	0.79	0.31	62.2	0.46	26.5	7.8	1.6	8.2	1600	3.3	55	42
400/10	0.71	0.28	63.9	0.44	26.5	8.3	1.4	7	1200	1.2	59	40
450/5	0.69	0.25	67.3	0.51	26.7	6.0	1.0	7.5	1600	0.9	44	55
400/20	0.66	0.24	67.8	0.52	27.7	6.6	1.3	7	1200	0.4	55	44
550/2	0.65	0.27	64.2	0.54	24.5	8.4	0.68	7.5	530	0.9	44	55
700/1	0.64	0.23	66.1	0.46	19.6	9.6	1.7	8.2	1100	0.5	43	57
450/10	0.59	0.26	65.9	0.62	23.8	7.5	0.94	7.8	520	0.1	46	54
450/20	0.58	0.20	68.9	0.53	25.5	8.9	1.1	8.1	650	0.1	46	53
500/5	0.56	0.21	68.5	0.49	22.9	8.8	1.3	8	300	0.0	38	62
600/2	0.54	0.24	67.2	0.51	21.2	7.7	1.6	8.4	470	0.1	24	76
500/10	0.49	0.20	69.1	0.50	22.2	9.6	0.95	8.1	240	0.0	19	81
550/5	0.45	0.21	68.9	0.47	20.6	8.9	0.90	8.2	130	0.0	3.5	96
650/2	0.45	0.19	68.9	0.55	18.6	10.2	1.8	9.5	160	0.0	3.9	96
500/20	0.44	0.21	68.4	0.49	20.4	9.7	1.4	8.6	150	0.0	2.9	97
550/10	0.43	0.22	66.8	0.49	18.8	11.0	1.5	9.2	230	0.0	1.0	99
600/5	0.41	0.17	70.4	0.50	20.4	10.4	1.6	9.2	71	0.0	1.7	98
550/20	0.40	0.21	69.1	0.49	19.0	9.2	1.3	9.3	22	0.0	1.3	98
700/2	0.39	0.15	70.9	0.47	16.7	11.7	1.9	9.2	75	0.0	4.5	96
600/10	0.37	0.16	71.6	0.40	19.8	10.2	1.6	9.4	21	0.0	1.3	99
650/5	0.35	0.25	64.2	0.43	16.7	12.5	1.5	9.6	21	0.0	1.0	99
600/20	0.34	0.15	72.8	0.46	18.8	10.4	1.8	9.5	40	0.3	0.5	99
650/10	0.31	0.16	71.7	0.44	17.5	10.7	1.5	9.4	6.4	1.1	0.7	98
650/20	0.29	0.15	71.8	0.44	17.8	11.8	1.8	9.9	1.6	1.5	1.1	98
700/5	0.28	0.11	75.4	0.40	15.7	11.3	1.9	9.6	4.4	0.9	1.5	98
700/10	0.26	0.18	69.8	0.40	16.8	11.9	2.1	9.8	1.8	0.0	1.8	98
700/20	0.25	0.13	73.4	0.39	17.3	12.3	2.0	10.2	0.4	0.0	0.0	100

Table 2
Correlation matrix of data reported in Table 1. Values from Py–GC–MS are italicised.

	H/C	**O/C**	**C**	**N**	**Char yield**	**Ash**	**PAH**	**pH**	***Py–GC yield***	***holocellulose***	***Lignin***
O/C	0.975										
C	−0.973	−0.992									
N	−0.617	−0.686	0.656								
Char yield	0.959	0.979	−0.953	−0.695							
Ash	−0.959	−0.913	0.902	0.505	−0.894						
PAHs	−0.777	−0.756	0.750	0.307	−0.760	0.790					
pH	−0.935	−0.867	0.872	0.424	−0.850	0.948	0.844				
Py–GC yield	*0.974*	*0.974*	*−0.960*	*−0.715*	*0.970*	*−0.916*	*−0.741*	*−0.868*			
Holocellulose	*0.934*	*0.970*	*−0.949*	*−0.774*	*0.957*	*−0.869*	*−0.648*	*−0.786*	*0.953*		
Lignin	*0.755*	*0.622*	*−0.652*	*−0.211*	*0.589*	*−0.791*	*−0.645*	*−0.869*	*0.656*	*0.519*	
Charred	*−0.929*	*−0.848*	*0.861*	*0.468*	*−0.819*	*0.929*	*0.735*	*0.952*	*−0.866*	*−0.785*	*−0.936*

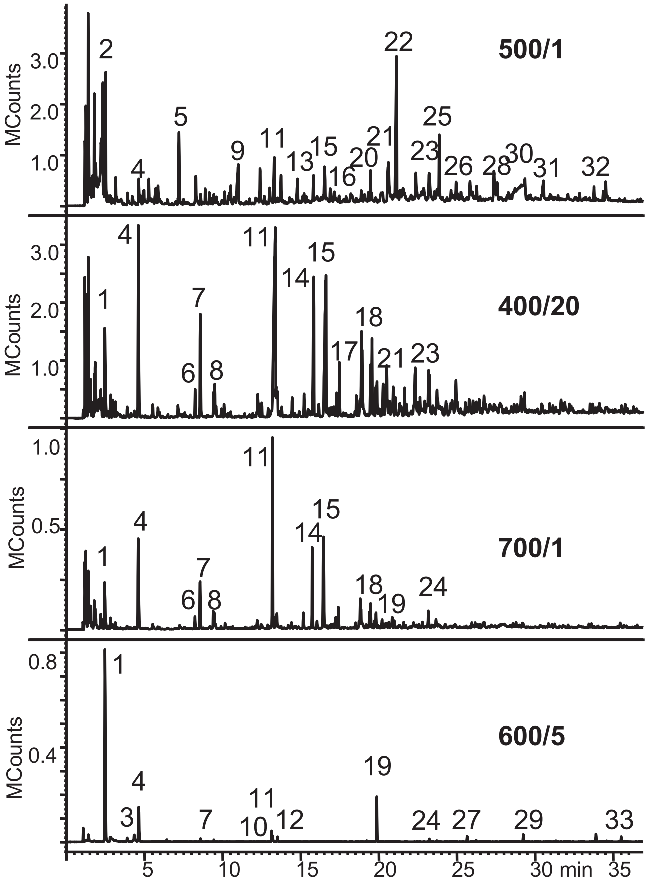

Fig. 1. Total ion chromatograms from Py–GC–MS of biochar 500/1 (0.51 mg), 400/20 (5.37 mg), 700/1 (0.53 mg) and 600/5 (5.21 mg). Peak attribution: 1: benzene; 2: hydroxyacetone; 3: pyrrole; 4: toluene; 5: furaldehyde; 6: ethyl benzene; 7: *m*/*p*-xylenes; 8: styrene; 9: 1,2-cyclopentanedione; 10: benzonitrile; 11: phenol; 12: benzofuran; 13: 3-hydroxy-2-methylcylopentenone; 14: *o*-methylphenol; 15: *m*/*p*-methylphenols; 16: guaiacol; 17: methylbenzofurans; 18: C2–phenols; 19: naphtalene; 20: 4-methylguaiacol; 21: cathecol; 22: 4-vinylphenol; 23: methylcathecols; 24: methylnaphthalenes; 25: 4-vinylguaiacol; 26: syringol; 27: biphenyl; 28: *trans*-isoeugenol; 29: dibenzofuran; 30: levoglucosan; 31: 4-vinylsyringol; 32: 4-propenylsyringol; 33: phenanthrene.

hemicellulose [38], could not be unambigously identified in the pyrolysates. Levoglucosan was the only anhydromonosaccharide positively identified in some pyrolysates (Fig. 1). The set of pyrolysis products of polysaccharides selected in this study could not be assigned specifically to cellulose or hemicellulose, thus this group was generically ascribed to holocellulose. However, the pyrolysis product 2-hydroxymethylenetetrahydrofuran-3-one, often identified as a hydroxypyrone [38], was indicated as a specific product of xylans [38,39].

The quantity of evolved pyrolysis products was expressed in terms of "yield" to give a rough estimate of the mass fraction that was analysed by GC–MS. Table 1 shows that the summed yields covered a large interval ranging from 0.4 $\mu g\,g^{-1}$ (700/20) to 7000 $\mu g\,g^{-1}$ (400/1). These orders of magnitudes are in accordance to data obtained under similar conditions from different biochars [17] and indicate that only a very small fraction of biochar could be thermally fragmented and analysed by GC–MS. The Py–GC–MS yields were strongly correlated with H/C and O/C ratios ($R = +0.97$ in both cases, Table 2) confirming earlier studies that the quantity of the evolved pyrolysis products is an inverse index of the charring intensity [13–15]. Analogously, the % charred fraction was correlated with the content of carbon ($R = +0.86$), ash ($R = +0.93$) and inversely correlated with H/C ($R = -0.93$) and O/C ratios ($R = -0.85$). A weak positive correlation was found between PAH levels and %charred ($R = +0.73$).

The molecular compositions of the pyrolysates were found to be significantly different in the investigated biochars. Pyrolysis products associated to cellulose (e.g. 2,5-dimethylfuran) and lignin markers preserving methoxy groups (e.g. guaiacols) became undetectable at H/C < 0.6 as evidenced in Fig. 2 showing the mass pyrograms of some biochars with decreasing H/C ratios. Less specific markers of lignin (methylphenols) were not detected in biochars with H/C < 0.4, but phenol was revealed in biochars with H/C ratios down to 0.3. Thus, the role of phenols and cathecols as markers of highly or weakly pyrolysed lignin is not that clear as discussed by Kaal et al. [15].

As far as the presence of markers of the highly carbonised faction is concerned, benzene, toluene, styrene and naphthalene were the only products revealed in the pyrolysates of all the samples, including the most charred biochar (700/20, H/C = 0.25). Benzonitrile, xylenes, benzofuran, pyrrole, ethylbenzene, biphenyl, and phenantrene were the other major pyrolysis products characterising biochars with H/C < 0.4. However, peak integration was difficult for highly carbonised biochars (H/C < 0.3) and artefacts due to cross-contamination may occur (for instance, weak signals of carbohydrate markers were detected in biochars 650/10 and 650/20). The relative content of pyrolysis products indicative of the more thermally altered fraction (% charred, Table 1) increased from about 10% for weakly charred biomass to 100% and was strongly correlated with the H/C ratio ($R = -0.93$).

Pyrolysis product yield ratios were calculated with respect to benzene, toluene and naphthalene because these were the only quantifiable compounds in the pyrolysates of the most charred biochars. Compound ratios with naphthalene gave better parameter correlations than with benzene or toluene, thus only the results relative to product/naphthalene ratios will be presented and discussed. Table SM1 reports the linear correlation coefficients of pyrolysis product/naphthalene ratios with char characteristics. Significant correlations with H/C ratios were found for benzofuran/naphthalene ($R = +0.93$),

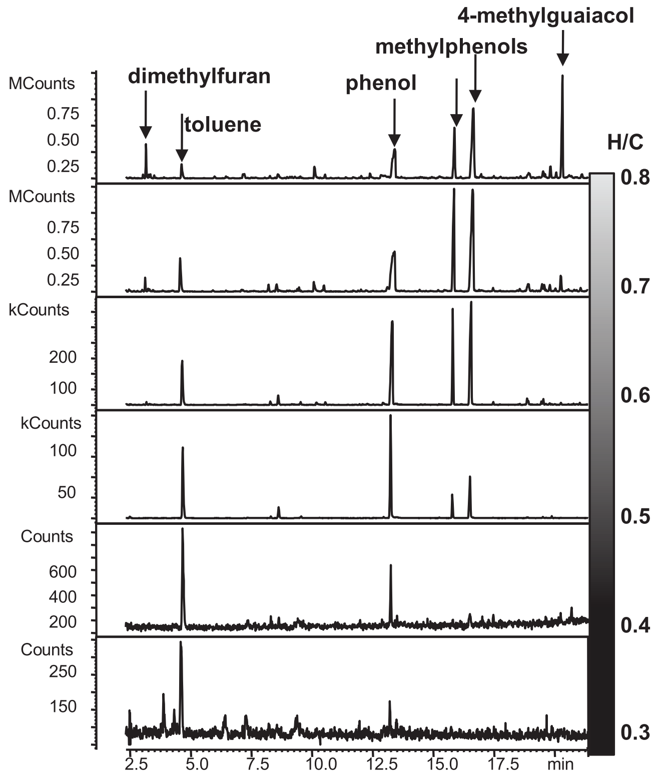

Fig. 2. Mass pyrograms at ions characteristics of toluene/phenol, dimethylfuran, methylphenols and 4-methylguaiacol at m/z 65, 96, 108 and 138, respectively. From top to bottom: Py–GC–MS of biochar samples 400/5, 450/5, 450/10, 500/10, 550/20, 700/2 and 650/10 and the corresponding H/C molar ratios.

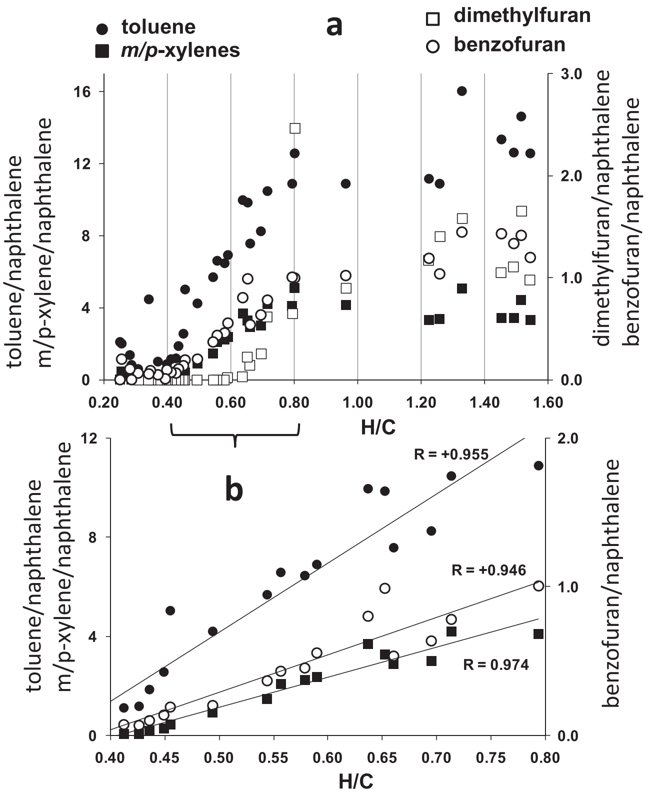

Fig. 3. Py–GC–MS yield ratios of selected pyrolysis products with naphthalene (a) in the whole and (b) in a selected H/C molar ratio interval.

toluene/naphthalene ($R = +0.89$), dimethylfuran/naphthalene ($R = +0.80$) and m/p-xylene/naphthalene ($R = +0.78$). These specific product/naphthalene ratios were directly correlated with O/C ratios, and inversely correlated with ash, PAH and pH values. The trends of these ratios with H/C were depicted in Fig. 3a. Benzofuran is a marker representative of oxygenated char components formed from the carbonisation of cellulose [40], alkylated benzenes of the labile fraction containing aliphatic domains [15], and naphthalene of polycondensed aromatic structures. Thus, these ratios describe the relative proportion of labile with the respect to recalcitrant fraction and accordingly decrease with increasing charring. A closer inspection to the pyrolysis product ratios vs. H/C showed that the linear relationships become stronger for biochars with H/C in the 0.8–0.4 interval, as exemplified in Fig. 3b. When calculated for these biochars, correlation coefficients increased to $R > +0.90$ ($n = 27$) for the pyrolysis product ratios of toluene, m/p-xylene and benzofuran with naphthalene. The dimethylfuran/naphthalene ratios decreased almost linearly with decreasing H/C ratios down to 0.6 where cellulose markers were not detected in the pyrograms. The benzene/toluene ratio utilised in other studies [15,17] was loosely correlated with H/C ($R = -0.45$), while the toluene/benzene ratio was better correlated ($R = +0.66$). Pyrolysis ratios of nitrogen-containing compounds, pyrrole and benzonitrile, with naphthalene were not correlated with the content of nitrogen; however, the benzonitrile/naphthalene ratio was weakly correlated with H/C, pH and ash.

3.3. Degradation in soil

Degradation tests were performed on four biochar samples characterised by different Py–GC–MS traces (Fig. 1). A principal component analysis was performed with the data set of Table 1 as variables (columns) and biochar samples as objects (rows) to better collocate the biochars in the collection. The first two principal components PC1 and PC2 accounted for the 83% and 10% of the variance, respectively, the former one dominated by data from Py–GC–MS and H/C. The plot of PC1-PC2 (reported in Figure SM1 of Supplementary materials) confirmed that the char variability was affected by pyrolysis conditions. Chars produced under mild process conditions (400–600 °C/1 min, 400–450 °C/2 min) formed a well segregated group (H/C > 1, Py–holocellulose > 10%); two less separated groups could be identified with H/C 0.49–0.80 (Py–lignin > 10%) and H/C 0.25–0.45 (Py–charred > 90%). Samples belonging to each group were selected for degradation studies: the two chars produced at the extremes in the temperature and time charring conditions (400/20 and 700/1), a weakly (500/1) and highly charred sample (600/5). The percent fraction of carbon C evolved as CO_2(C–CO_2) relative to the initial C-biochar as a function of time is reported in Fig. 4. This fraction was assumed to correspond substantially to the mineralisation of organic C, since the

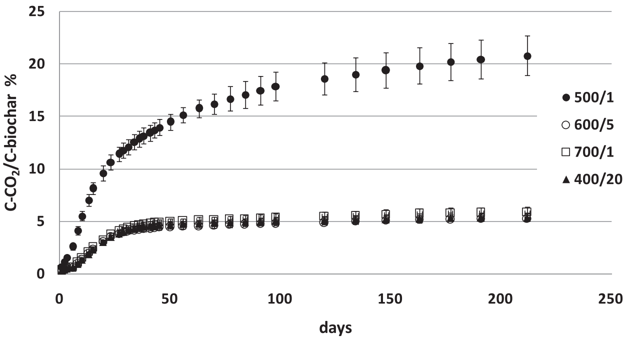

Fig. 4. Net cumulative CO_2 loss (% of initial carbon) from soil mixed with biochar samples 400/20, 500/1, 600/5 and 700/1 (mean values and s.d. from three replicates).

contribution from inorganic C (carbonates) should be minimal owing to the rather low ash content. The CO_2 production observed after 220 days was 20.8 ± 3.7% for soil mixed with biochar 500/1. It can be noted that 50% of the final degradation was measured after only 23 days. The maximum degradation rate (0.75% day^{-1}), given by the slope of the tangent to each curve, was measured in the first two days, then the degradation rate progressively decreased down to a value of about 0.03% day^{-1} after 6 months.

After 7 months biochar 600/5 showed a total CO_2 production of 5.2 ± 0.72%, much smaller than that measured in sample 500/1. Moreover, at the end of the experiment the degradation rate (if any) was extremely small. Half of the total CO_2 production was measured after about 17 days. Also in this case the maximum degradation rate (0.33% day^{-1}) was observed at the beginning of the process. A similar behaviour was observed for intermediate biochars: the extent of degradation resulted to be 5.4 ± 0.92% and 5.8 ± 1.2%, with maximum rates of 0.29% and 0.40% per day, for samples 400/20 and 700/1, respectively. In general, the production of CO_2 did not require an induction period, and the maximum degradation rate was reached within the first two days, followed by a gradual decrease.

The values of the total emissions of CO_2 were comparable to those reported by Bruun et al. [41] for biochars obtained with fast pyrolysis of wheat straw, that is from 12 to 3.1% in 115 days of initial C for the lowest (475 °C) and highest (575 °C) pyrolysis temperatures, respectively. Interestingly, this study found a strict linear relationship between cumulated CO_2 emissions and the content of cellulose and hemicellulose remaining in the biochar due incomplete biomass conversion of the employed fast pyrolysis process [41]. Lower values of CO_2 emissions were reported by Zimmerman [19], but in rather different conditions (e.g. sand in place of soil).

It was suggested that the recalcitrance of biochar is related to O/C ratios [20]. When O/C ratio is greater than 0.6, then biochar will probably possess a half-life time on the order of less than 100 years, while 100–1000 years may correspond to biochar with O/C ratio between 0.6 and 0.2. In this study, the most labile biochar had a O/C ratio of 0.73, while the other three biochars had O/C ratios between 0.17 and 0.25 and showed similar recalcitrance to degradation. Interestingly, the molecular patterns emerged from Py–GC–MS of the four biochars were rather different (Fig. 1, Table 1). The pyrolysate of the most labile biochar contained a significant proportion of holocellulose (39%) and lignin (50%) markers. The pyrolysates of the other biochars had very low levels of holocellulose markers (<1%) and were characterised by different proportions of lignin markers (1.7–55%). Thus, the main difference between the biochars with high and low degradation rates was the significant presence of polysaccharide markers in the former. In a previous study it was observed that biochars producing pyrolysates rich in holocellulose markers were characterised by high CO_2 emissions [17].

The identification of 2-hydroxymethylene tetrahydrofuran-3-one in the pyrolysates of samples with $H/C > 1$ suggested the presence of partially charred hemicellulose [39], while the occurrence of levoglucosan indicated partially degraded cellulose (Fig. 1). It is known that hemicellulose starts decomposing at lower temperatures than cellulose, and for switchgrass the peak temperature of hemicellulose degradation was below 315 °C and higher than 340 °C for cellulose [36]. Cellulose is more stable towards charring than hemicellulose [41], moreover in the pyrolysis of mixed cellulose–hemicelluloses, cellulose is covered with the molten hemicellulose layer before pyrolysis reaction starts in cellulose [39]. Therefore, one can expect that hemicellulose is more thermally degraded than cellulose under the same conditions, however, char from hemicellulose (xylan) is formed at higher yield than from cellulose and with a higher oxygen content [42].

Altogether these findings would indicate that the propensity of biochar to short-term degradation is governed mostly by the presence of weakly charred cellulose and hemicellulose. However, the effect of process conditions, such as fast [41], slow [19] and intermediate pyrolysis (this study) on biochar characteristics (particle size, bio-oil residue) should be considered in comparative studies and caution exercised in generalisations.

Besides the characteristics of biochars, their yields should be taken into account when considering the optimisation of pyrolysis conditions. The percentage fraction F of carbon degraded to CO_2 in comparison to the original carbon in the biomass was calculated with the following equation:

$$F = \left(\frac{\text{C-CO}_2}{\text{C-biochar}}\right) \times \text{yield} \times \left(\frac{\text{C-biochar}}{\text{C-biomass}}\right)$$

By using the figures reported in Table 1 the following values were obtained: 19% (500/1), 2.4% (400/20), 1.8% (700/1), 1.8% (600/5). These data would suggest that the synthesis of a highly carbonised biochar is not a strong requisite for sequestration purposes, provided the H/C ratios are below a given value (<0.7 in the present study) and low pyrolysis temperatures could be preferred in the balance, as evidenced by Masek et al. [43].

In the present study, recalcitrant biochars with H/C ratios below 0.7, when holocellulose markers and methoxyphenols were not detectable, could be obtained with short residence times and sufficiently high temperatures. Relatively short residence times are generally suitable for small reactors and reduce the energy consumption, as discussed in [24] for switchgrass biochars obtained from pyrolysis with a fixed-bed reactor at short residence times (2.5 and 5 min). Analogously in the case of fast pyrolsys, it was suggested that a low extent of pyrolysis could be effective to produce biochars stable to biodegradation [44].

4. Conclusions

The results of this study conducted on a large set of samples produced from the same feedstock and reactor unit demonstrated that the GC–MS analysis of the tiny fraction produced by analytical flash pyrolysis can provide molecular indices useful for the interpretation of the thermal and environmental stability of biochar. The quantity of evolved pyrolysis products, the relative abundance of pyrolysis products associated to charring, and selected pyrolysis product ratios were strongly correlated with H/C and O/C ratios. The pyrolysates of biochars with H/C ratios above 0.8 were characterised by typical pyrolysis products of holocellulose (dimethylfuran) and lignin (methoxyphenols) and the dimethylfuran/naphthalene ratio was linearly correlated with H/C ratios. The toluene/naphthalene, benzofuran/naphthalene and *m*/*p*-xylene/naphthalene ratios were linearly correlated with H/C ratios in the 0.8–0.4 H/C ratio interval. This finding suggested that alkylbenzenes and benzofuran are proxies of aliphatic and oxygenated structures composing the most degradable fraction of biochar, while naphthalene is representative of polycondensed units that are more resistant to thermal degradation. In the 0.7–0.4 H/C range, the investigated biochars exhibited a moderate and comparable resistance to aerobic degradation. At lower H/C ratios, the intensity of pyrolysates of biochars was weak and few pyrolysis products could be detected.

In summary, the thermally labile fraction of biochar could be classified into three categories (obviously the reported values are not clear cut boundaries):

- weakly charred, thermochemical alteration minimal, molecular markers of holocellulose and lignin (methoxyphenols) clearly detected, % charred < 30% (biochar with $H/C > 0.8$);

- moderately charred, holocellulose markers not detected, methylphenols detected, % charred 40–80% (biochar with $0.4 < H/C < 0.8$);
- highly charred, pyrolysates dominated by markers of charring (>90%) (biochar with $H/C < 0.4$; with $H/C < 0.3$ the biochar could not be fragmented into GC–MS analysable products by flash pyrolysis).

Although the number of samples on which soil respiration experiments were conducted was low to infer robust conclusions, the obtained results suggested that biochars belonging to the intermediate category exhibited similar environmental stability. Biochars with a degree of carbonisation consistent with environmental recalcitrance could be obtained at relatively mild synthesis conditions, that is low charring temperatures or short residence times. The optimal process conditions could be rapidly investigated by Py–GC–MS utilising the appropriate molecular proxies. The proxies proposed in this study emerged from the analysis of a single substrate (switchgrass) and pyrolysis system, further research is needed to attest their general validity and elucidate relationships across different feedstock and pyrolysis units.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jaap.2014.09.010.

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